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Temperature Control of an Emulsion Polymerization Process

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Executive Summary

Temperature control of an emulsion polymerization batch is crucial for final product quality such as crosslinking when using diene monomers such as 1,3 butadiene. Proportional-Integral-Derivative (PID) control works well for incremental batch emulsion polymerization but still has problems with deviating too far from the set point of the batch as the monomer is added in multiple steps. The PID control cannot predict the disturbances of monomer charges throughout the batch. The charges of monomer throughout the batch reduce the batch temperature. Also, the PID control cannot predict exothermic reaction which causes the batch to heat itself. The cooling and heating of the batch cause the PID control to respond and return the batch temperature to the set point but this does not happen before large dips and rises in temperature occur causing a large deviation in temperature of the batch. The goal of this study was to develop a new method of temperature control to better track the batch set point of incremental batches through the incremental charges and to avoid overshoot of the batch temperature. The new control scheme would provide consistent particle size and better product quality.

The project focused on developing three different parameters for an incremental emulsion polymerization batch at the pilot plant scale. A method for the collection of data for the rate of change (ROC) was studied first. Measuring the temperature over time and subtracting the differences in temperatures to develop an ROC proved to be very inconsistent due to the noise present in electronic measuring devices. Research into various data filtering methods resulted in the use of the Savitzky-Golay data filter as the most accurate and best option for data filtering. A 6 parameter equation was introduced into the computer system to filter the data and create a smoother ROC for the temperature of the reactor. The data filter was able to use 6 data points

collected 10 seconds apart to generate an average value for the ROC and more accurately represent the emulsion polymerization batch.

The second parameter that needed to be addressed was the state of the jacket mode which can be categorized into three actions: cooling, heating, and recirculation. A dead band had to be created around the set point of the emulsion polymerization batch as the primary condition for determining the mode of the jacket. Once the batch temperature fell within the dead band, the ROC measurement made sure the batch was not heating or cooling at a fast rate. If the rate of change of the batch temperature was too fast, heating or cooling was activated to avoid overshoot of the set point. If the batch dropped below the lower dead band limit around the set point, the heating would be activated for the jacket to raise the temperature of the batch. If the batch rose above the upper dead band limit around the set point, the cooling would be activated for the jacket to cool the batch temperature. Inside the dead band limits, the reactor would remain in recirculation mode which meant the heating and cooling would be turned off. If the ROC measurement was too high while inside the dead band, the heating or cooling would turn on in order to ensure the batch temperature did not overheat or under-cool.

The last parameter that needed to be addressed was clamping the jacket. The emulsion polymerization batch responded quickly to heating but did not respond as quickly to cooling. The cooling would remain on the jacket fluid bringing the jacket temperature almost 40°F below the set point. Once the batch temperature finally dropped into the dead band limits around the set point, the jacket could not warm up quickly enough to stop the batch temperature from continuing well below the lower dead band limits. A clamp on the jacket needed to be installed in order to prevent the jacket fluid from dropping so low and the batch temperature dropping

below the lower dead band limit. This lower limit was determined using a conductive energy balance between the jacket fluid temperature and the batch temperature.

After performing tests on the pilot scale, a set of parameters was determined to be ideal for the incremental emulsion polymerization batches. A ROC of + 0.5°F per minute for heating and 0.5°F for cooling was ideal to ensure that, in the dead band limits of the set point, the batch did not continue to quickly rise or fall out of the dead band. The dead band limits for the pilot scale reactor was +/- 2°F which led to quick responses from the jacket if the batch temperature fell out that range without causing the heating and cooling to constantly be working and recirculation mode could maintain a more constant temperature. The jacket clamp was set at 17.5°F which meant that the jacket fluid would not heat higher than or lower than 17.5°F of the set point on the batch.

The results of the added parameters generated an effective temperature control scheme that was able to counter-act the monomer additions and exothermic reactions in a quick and timely manner. This new control scheme minimized batch temperature deviations from the set point which in turn improved the particle size control and product quality. Additional studies need to be conducted before the control scheme can be added to a production facility. The parameters will need tuned to the larger reactors found in a production plant since the ratio of the polymer material to the jacket fluid is much greater on a larger scale.

The project has allowed for me to learn a great deal behind the computer system running the polymer batches at a Pilot Plant and Production facility that creates emulsion polymers, or latex. Working alongside engineers with vast knowledge about the computer system has been a huge help in the development of my becoming a chemical engineer. By having a wide variety of knowledge, I will be able to troubleshoot problems in various areas of a plant as well as

understand how the electronics and control systems of a plant are incorporated to work with one another in series and parallel to create a temperature control scheme.

In addition to the knowledge about the electronics and controls of a process, I also became very familiar with the equipment, materials, and utilities involved in creating an emulsion polymer batch. To better understand what was happening in the plant with the reactors, I spent many hours alongside the TCU and reaction vessel learning to run batches, repair equipment, and watch live data collection in order to fully understand how each piece of the process is critical to create a product. Looking at the equipment and understanding connectivity was only a part of learning the equipment. I also had to spend time looking over the drawings and equipment specifications to determine jacket volume and steam and cooling water temperatures to help determine ideal jacket clamp temperatures and to guess how quickly the batch would respond to heating or cooling.

1.0 Background

1.1 General Emulsion Polymerization Process

The emulsion polymerization process utilizes monomer, surfactants, water, and other raw materials to create latex; latex is a general term for polymer suspended in an aqueous medium. Emulsion polymerization was developed during World War II as a replacement for natural rubber which was in short supply in the United States[1]. The process of emulsion polymerization is a radical addition polymerization that uses the hydrophobic tendency of monomer in water to create an emulsification. The water provides a medium for heat transfer and contains the dispersed monomer particles that create the final latex product.

The polymer chain can be built in three different methods depending on the desired final product. The first method is an all-in batch. As the name implies, an all-in batch adds all of the monomer, surfactant, and initiator at the start of the batch and allowing the monomer to react into the polymer chains until the monomer has been consumed and the reaction stops. This method can builds higher pressure at the beginning of the batch if a liquefied monomer such as 1,3 butadiene is used. Over time the monomer polymerizes and the pressure decreases. If 1st order kinetics for monomer consumption is assumed, an all-in batch polymerization for emulsion polymerization liberates a large amount of heat during the initial conversion of the monomer to polymer. Temperature cycling normally occurs since the PID controller cannot handle the sudden change in batch temperature.

The second style of batch that can be run on the process is the incremental batch method. The incremental batch breaks the monomer and surfactants into separate additions in order to better control the temperature of the batch. The monomer cannot be pre-heated to the reaction temperature due to the potential for the monomer to react with itself. As a result, the temperature

of the batch drops a few degrees once the monomer is added and the control system responds to heat the batch back to the desired temperature. During this heat up, an exothermic reaction raises the temperature well above the set point causing the jacket to turn to cooling. These heating and cooling cycles causes a significant deviation to the batch temperature.

The third method of emulsion polymerization is done by a semi-continuous method of monomer addition. The semi-continuous method involves a constant flow of monomers and the other raw materials over a set amount of time. The constant flow of monomer means that it enters the system very slowly compared to the whole amount of monomer that goes in the batch. This method helps to control batch temperature the best because of the slow addition of monomer and predictable heat control. The constant addition means that the heating system accurately can track the set point of the batch with minimal fluctuation and deviation. Since the monomer is constantly added, the reaction is not starved of monomer and the potential for uneven distribution of monomers into the polymer backbone.

1.2 Emulsion Polymerization Process Used for Study

The emulsion polymerization process used for the temperature control system is presented in a very basic picture presented in figure 1. The reactor is a stainless steel reactor that is surrounded by an insulated jacket. The insulated jacket contains ethylene glycol that is used for heat transfer. The reactor has a cylindrical shape with a curved top and bottom. The jacket surrounds the reactor on all sides except for the top portion of the vessel which has the curved shape. The reactor contains multiple ports on the top and bottom of the vessel that contain pressure sensors, temperature sensors, nitrogen lines, vacuum lines, and steam lines. The sensors monitor the conditions of the batch. The nitrogen, vacuum, and steam lines are used for

preparing the reactor, cleaning the reactor, and transferring the batch at its completion. An agitator on the top of the reactor ensures the best possible mixing of the reactor contents in order to make sure the polymerization reaction occurs uniformly. A raw material header is present on the top of the reactor where the materials are charged to the vessel. All of the raw materials are fed into this one header so only one port is required on the top of the reactor.

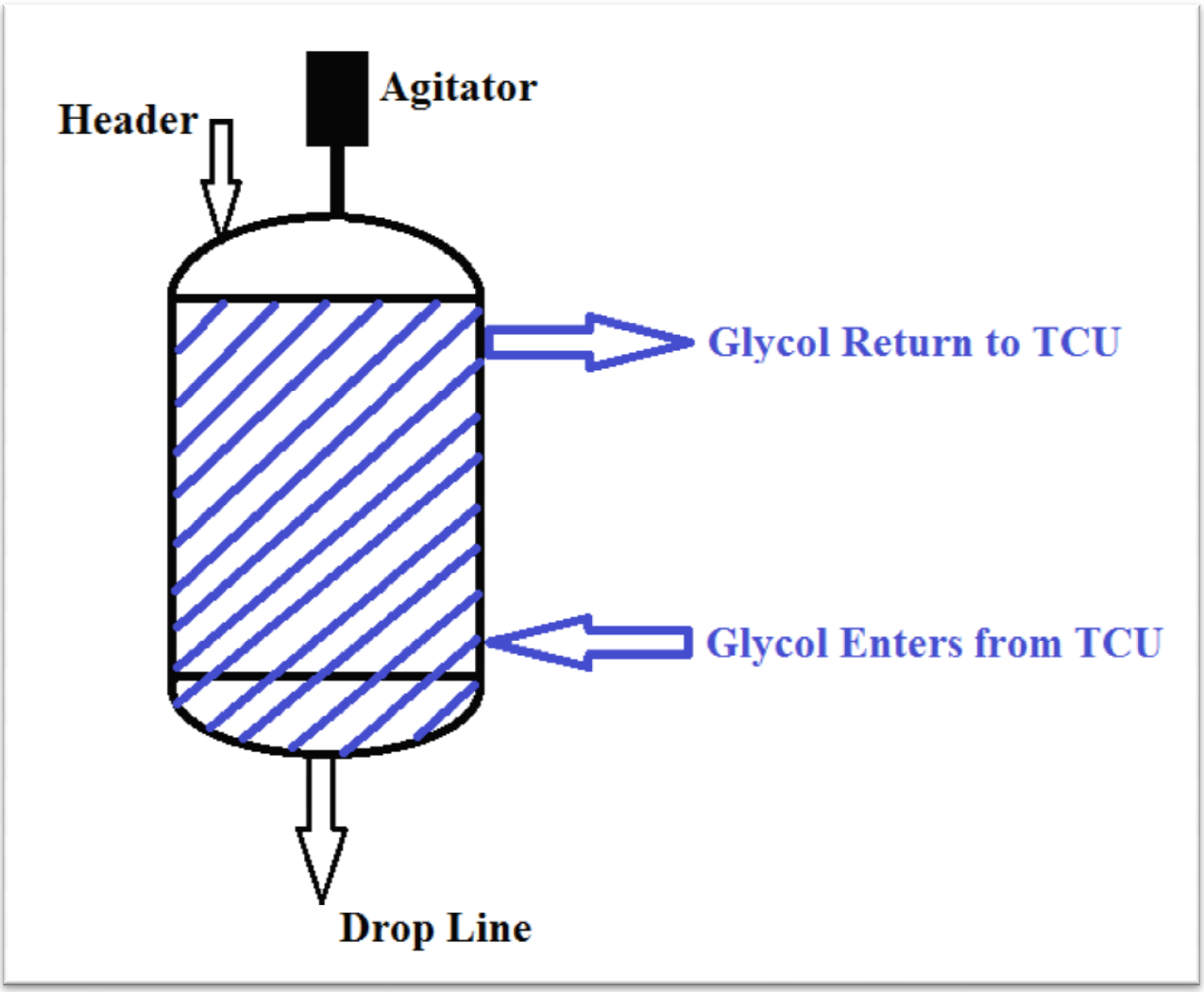

Figure 1. Picture of the basic reactor setup used in the emulsion polymerization process. The diagonal blue lines indicate the region of the vessel that is jacketed where the glycol is pumped through to either heat or cool the batch depending on the desired set point. The header is the location where the raw materials are pumped into the vessel. The agitator provides ample mixing for even heat exchange as well as material dispersion.

The jacket on the vessel is filled with 50% ethylene glycol and water mixture which acts as the heating and cooling fluid. The ethylene glycol mixture has a boiling point of 225°F and a melting point of 34°F which makes it a good choice for being in the jacket since the polymerization process does not get anywhere near those high and low transition temperatures.[2] The glycol travels from the jacket around the vessel to a temperature control unit (TCU). The glycol returns to the TCU where it passes through the first heat exchanger. Steam is used to heat the glycol mixture in the first heat exchanger of the TCU. The steam enters the plant at 90 pounds per square inch-gauge (psig) which, according to steam tables, is around 340°F. Before it enters the TCU the steam is reduced to about 40 psig. This pressure reduction superheats the steam. The steam is on the inside of the U-tube heat exchanger and the glycol mixture passes on the shell side of the exchanger.

The glycol mixture then passes through the second heat exchanger which is the cooling heat exchanger. The second heat exchanger uses chilled water. Chilled water goes through a cooling system reducing the temperature to 50°F. The glycol mixture passes on the tube side of the U-tube heat exchanger while the chilled water runs on the shell side of the exchanger. A control valve on both the steam and the cooling water constitute whether or not steam or cooling water is allowed to flow through the exchangers. The controller logic stipulates that only one of the utility valves can be open at any given time in order to avoid both heating and cooling the glycol mixture at the same time. After passing through the second heat exchanger, the glycol mixture then returns to the jacket.

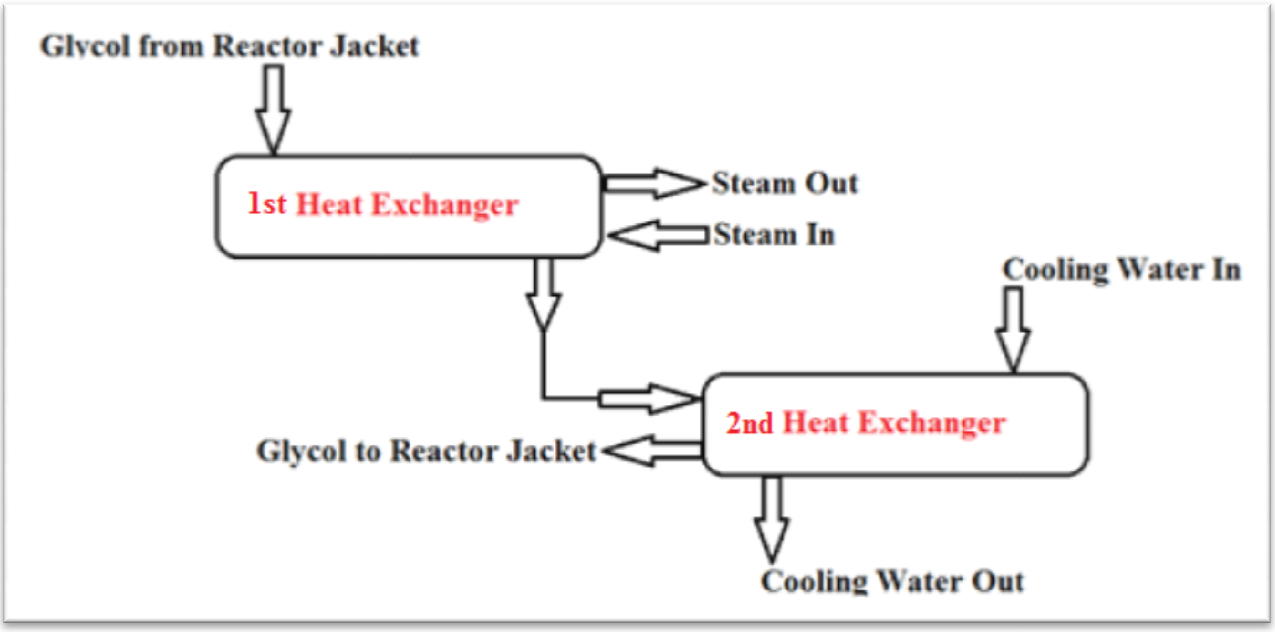

Figure 2. Picture of the TCU showing how the heat exchanger network is set up. The glycol travels from the reactor jacket to the TCU unit where it enters the first heat exchanger. The first heat exchanger is the steam exchanger which is used to heat the glycol mixture if the batch temperature drops. A control valve regulates steam flow into the vessel. The glycol mixture then leaves the heating exchanger then enters the cooling exchanger. The cooling water is regulated by a control valve. After the cooling exchanger the glycol mixture is then pumped back to the reactor jacket to either heat or cool the batch.

This study will use three different modes of the TCU to control the temperature of the batch. The TCU will either full heat, full cool, or be in recirculation mode. Full heat is where the steam valve opens 100% allowing maximum steam flow into the first heat exchanger to raise the temperature of the glycol mixture while the cooling water valve remains closed. Full cool means that the cooling water valve will open 100% allowing maximum flow of the cooling water to enter the second heat exchanger to cool the glycol mixture temperature while the steam valves remains closed. Recirculation mode is when both the steam and the cooling water valves remain closed and the glycol mixture is simply pumped from the jacket to the TCU and back with no additional heat transfer from the TCU other than between the glycol mixture and the polymer batch. Another added heat to the system is the energy added through the pump used to circulate

the glycol mixture. A dead band will be used to determine which state the jacket will be in. The dead band is a region above and below a set point in which the jacket will remain in recirculation mode with no heating or cooling needed.

1.3 Controls

Throughout the emulsion polymerization industry temperature is controlled by cascade control of the jacket where a proportional integral (PI) controller is implemented for the jacket and a proportional integral derivative (PID) controller is implemented for the batch. Proportional control adjusts the output signal in direct proportion to the controller input which is the error signal. Proportional mode still experiences some error and offset which is why Proportional-Integral is added to a system. PI systems add an integral mode which corrects for offset (error) that occurs between the set point and the process output. Proportional and PI control uses the process as the only means of adjusting control. Proportional-Integral-Derivative control anticipates where the process is headed because of the derivative portion of the controller. The derivative portion of a PID looks at the time rate of change of the controlled variable and makes adjustments in what the predicted response will be. The main problem with PID control is that disturbance and noisy signals can drastically affect the derivative portion of the controller and the response would be undesirable.[5]

Controllers for continuous and semi-continuous processes can be tuned as long as the input disturbances are not too large to disrupt the system. Incremental batch polymerization has troubles with temperature control because of the individual monomer additions. The incremental charges cool the batch significantly on a large scale and force a large response from the jacket which in turn heats the batch beyond the set-point. Once beyond the set-point the jacket will try to turn over to cooling to regain the set-point but by the time the jacket and vessel respond, the

temperature overshoots thus leading to a large cooling response. Additionally, the heat of polymerization is being liberated by the addition of monomer which assists in the overshoot of the set-point. Temperature control is crucial for ensuring the initiator continues to drive the polymerization reaction as well as controlling the reaction rate at which the polymer chains grow and increase in molecular weight.

1.4 Emulsion Polymerization Batches

A normal incremental batch has anywhere from 6 monomer additions to 14 monomer additions depending on the final properties. Figure 3 below shows an 8 monomer increment batch with a set point of 170°F. The initial ~200 minutes of the batch is the start-up portion of the recipe. In this portion of the batch, the initial seed monomer, water, and surfactants are added to the reactor and are heated up to a starting temperature so when the first addition of initiator is added, the polymerization process will begin. As the polymer begins to form, the batch is heated up to the 170°F to continue the reaction and monomer additions.

The monomer additions occur immediately before the pressure increases significantly, almost instantaneously, and the temperature of the batch drops. Figure 3 shows the monomer additions around 300 minutes, 375 minutes, 450 minutes, and so on at 75 minute increments. The pressure rises as the liquefied monomer such as 1,3 butadiene is pumped into the vessel and occupies the head-space of the reactor. The pressure then starts dropping once the polymer reaction proceeds, which is an indication of the monomer being consumed and joining the polymer chain. This can be seen right after the peaks in pressure on figure 3. Another indication of the monomer addition is when the batch temperature drops and the jacket responds by heating up. The monomer cannot be preheated because of the potential for it to self-polymerize and become unstable which could cause an accident. The cooler monomer reduces the batch

temperature so the control system responds and heats the jacket in order to heat the batch. On figure 3, the jacket begins heating around the same time the monomer additions are added. The reaction is exothermic so as the jacket is heating the batch, the batch itself is generating heat which then causes the batch temperautre to rise above the set point and the jacket then has to cool.

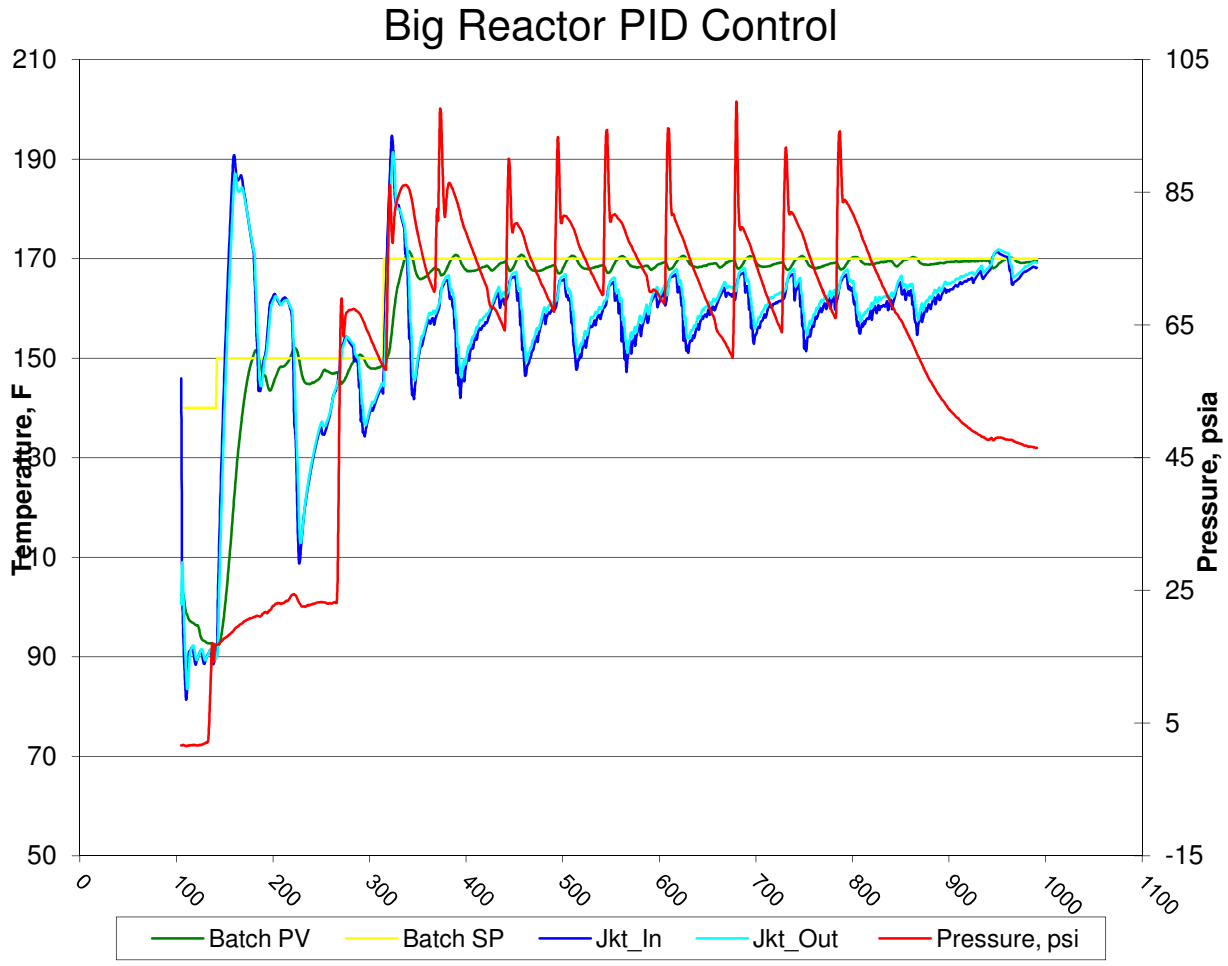

Figure 3. Chart of a normal incremental polymerization batch. Batch PV is the present value, or batch temperature; batch SP is the batch set point; Jkt In is the temperature of the glycol as it enters the jacket; Jkt Out is the temperature of the glycol as it leaves the jacket; and Pressure, psi is the pressure of the batch in pounds per square inch. Between 100 minutes and 300 minutes the batch is in the initial start-up part where the starting amounts of water and seed raw materials are added to the reactor and brought up to the starting temperature. The red line is the pressure and helps to identify when a reaction occurs. Once an incremental charge is made, the pressure instantly is increased and as the reaction ensues, as the pressure decreases, the monomer is

reacting out and forming polymer chains. The reaction can also be noted by the drop in batch temperature once the monomer is added, causing the jacket to begin heating the batch. The reaction is exothermic so the batch temperature begins to rise with the jacket and the jacket must start cooling the system.

An oscillation in the over-heating and over-cooling fluctuate the temperature too much for a polymerization process which can be affected by a 5°F change. My project is to implement an alternate method of incremental charge control where the temperature of the batch can be controlled using the same type of inputs the PID controller uses such as the rate of change of the temperature as well as the anticipation of the heat of polymerization of the incoming increment to prevent the temperature overshoot.

The plan for this controller is to:

1. Monitor the rate of change of the batch temperature.
2. Place the jacket in full heat, full cool, or recirculation based on the rate of change.
3. Create a dead band limit around the batch set-point to indicate the limits the TCU will remain in recirculation and if it exceeds those limits, the TCU will enter in full heating or cooling.

2.0 Monitoring the Rate of Change

Emulsion polymerization processes greatly depend on temperature control to ensure the extent of reaction and reaction rate are closely controlled. The polymerization reaction occurs in large reaction vessels to create the many latex products used in paints, wallpaper, carpeting, and many other products. In order to maintain a uniform temperature throughout the system, the polymer batches are agitated and heated using a jacketed vessel. The temperature control system for the jacket is a PI system and the batch uses a PID control system. The batch temperature is monitored using a thermocouple or RTD that transmits the electrical signal to the computer system. The PID control system uses the batch temperature to determine whether or not to allow heating or cooling to turn on and how open the control valve should be opened.

The rate of change would be a secondary measure on the temperature control system meaning once the temperature of the batch was within the dead band, then the rate of change would checked to make sure it too was within the range determined to be ideal. The new proposed system would use the rate of change (ROC) of the batch as well as a dead band around the desired temperature to control the jacket heating or cooling the batch. The rate of change was first recorded as a simple temperature difference divided by the sample time between one second measurements. The one second intervals yielded a very jagged set of data that had positive and negative spikes. These extreme spikes are caused by the noise associated with the thermocouple that is in the reactor which takes real-time temperature readings of the batch. The noise generated led to the rate of change to be highly unreliable for use in creating the new control system.

A data filtering method was needed in order to smooth out the rate of change. A smooth rate of change line would help to better control the heating and cooling of the jacket material instead of constant oscillations. A common digital filter that has been proved to be an effective

method to smooth data is the Savitzky-Golay filter. The Savitzky-Golay filter has the ability to increase the signal-to-noise ratio without distorting the signal [Source 2]. The filter uses convolution which fits successive sub-sets of adjacent data points with a low-degree polynomial by the method of linear least squares.

Abraham Savitzky and Marcel Golay, who the filter is named after, first published their paper on signal data filtering in 1964. A set of coefficients depending on the number of data points used creates a smooth line of the temperature differences. Each data point is replaced by a local average of the surrounding data points. The new, smooth data set is then able to be used to generate a new value for the rate of change. This smooth rate of change can then be used to help determine whether or not to place the temperature control unit (TCU) in heating, cooling, or recirculation mode.

A six co-efficient equation was chosen as the filter for smoothing the data. After implementing the Savtizky-Golay filter into the rate of change calculation, the sampling time had to be adjusted. Initially the data was collected in one second intervals. The sampling of every second still generated a noisy data set that was an improvement from the initial rate of change calculation; however it still was not accurate enough for the large reactor system. The sampling time was then increased to every minute. The increased sampling time improved the data smoothing and data was collected on a small reactor. However, from looking at the small reactor, the one minute sampling time was not effective in accurately reading the rate of change because the batch temperature quickly responded to jacket variations and the rate of change was delayed in responding to the negative change.

After altering the data collection time and performing tests on water-filled reactors, it was determined that a 10 second data collection was the ideal time spacing. Every minute had six

samplings which were frequent enough to maintain a smooth data set as well as respond to the actual changes in the reactor. The 10 second sampling worked for the different sized reactors which ranged from a couple gallons to hundreds of gallons. With this successful filter, the first part of the new controller was completed.

The ROC was tested on a simple water filled reactor in order to ensure the values were accurately tracked through the computer system. Figure 4 below shows the rate of change for three different sampling times. As stated before, the one minute sample for the ROC was the smoothest line of all which can be seen from the green line on the chart. The ten second data sampling is shown by the black line on the chart. The one second sampling interval is shown by the purple line on the chart. The one second sampling shows a highly fluctuating trend that follows the same general trend as the other two sampling methods, however it can flip almost a full degree per minute. The ten second sampling still has the slight bouncing around but not nearly as severe as the one second and it responds faster to the system than the one minute data sampling.

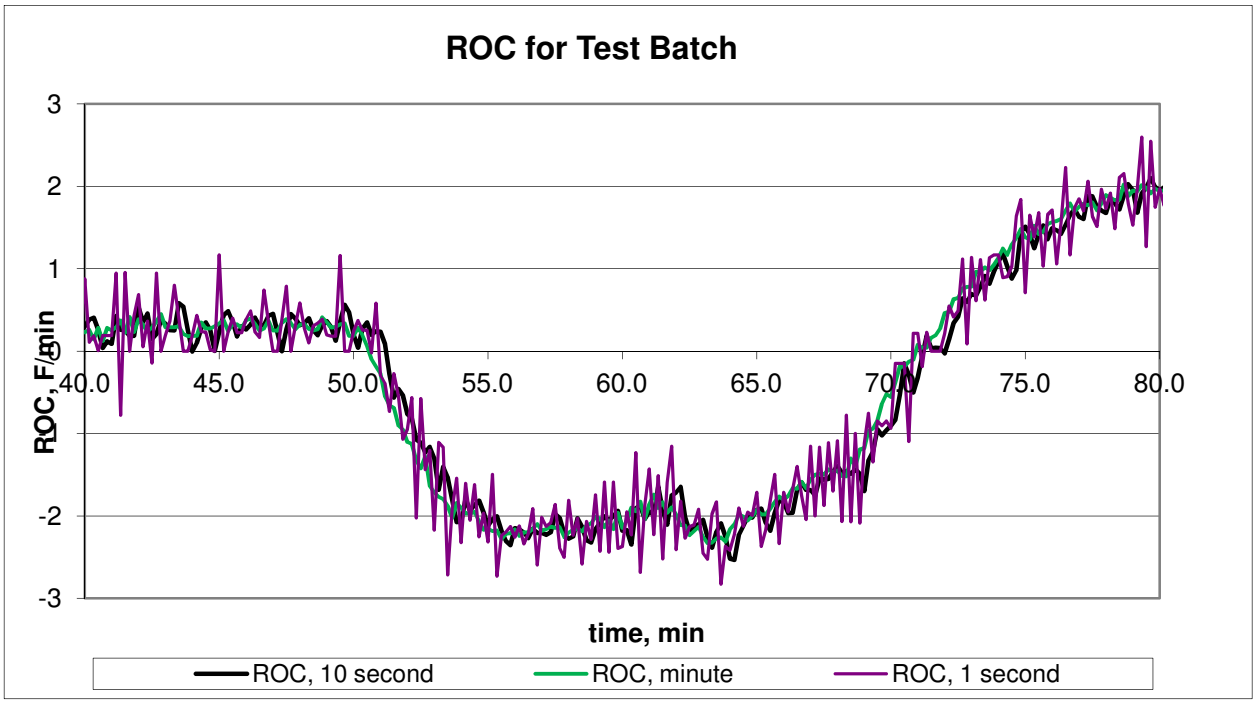

Figure 4. Chart showing the rate of change using the Savitzky-Golay filter for three separate sampling methods; one second, ten seconds, and one minute. The green line of the one minute sampling is the smoothest of the three lines, however, the response time to changes in the batch made one minute insufficient. The black line is the ten second sampling rate and shows some choppy behavior, however, with its relatively quick response and relatively smooth behavior, it was determined to be the ideal sampling value. The purple line is the one second sampling of the change in temperatures. The one second sampling quickly responded to variation in the batch temperature but the constant choppy behavior led to the response to be sporadic and inefficient.

3.0 Varying Jacket Modes

The goal of determining the rate of change was to make sure the system was not heating too quickly or cooling too quickly once the batch temperature was within the dead band. The ROC would place the temperature control unit (TCU) into full heating or full cooling if the batch temperature was still falling or rising too quickly. Full heating is done by completely opening the steam control valve and completely closing the cooling water control valve. This setting would allow the glycol mixture passing through the steam heat exchanger to heat up and begin raising the temperature of the batch. Full cooling would close the steam control valve and fully open the cooling water control valve so that the glycol mixture would not heat up passing through the steam heat exchanger and would be cooled by the cooling heat exchanger. In recirculation mode the steam control valve and cooling water control valve would both close and would circulate the glycol mixture through the TCU and reactor jacket and use the heat transfer between the batch and the jacket glycol to maintain a constant temperature.

Initially, a series of “and/or” logic statements were implemented that determined whether or not the steam and cooling water control valves would be full open or full closed. Parameters for the “and/or” statements were varied by tracking the temperature of the batch, the rate of change of the batch temperature, and the dead band to keep the temperature within the set point. At first a dead band range was set around the ideal set point of plus or minus (+/-) 5 degrees Fahrenheit to test the new system. Also, the rate of change for heat up was placed at 1 degrees Fahrenheit per minute and the rate of change for cool down was set at 0.5 degrees Fahrenheit per minute.

The first case of a range of +/- 5 degrees created a trend that was too much full cool and full heat. Once the temperature of the batch dropped below the 5 degrees below the set point, the

full steam to the TCU turned on. However, once the heat turned on full, the system took a while to heat the glycol mixture in the jacket system and heat the shell of the reactor based on data from the batch. By the time the reactor reached a temperature within the 5 degree range, the temperature of the glycol mixture was so high that it proceeded to carry the temperature of the batch well above the 5 degree above the set point temperature before the cooling finally kicked on and brought the batch down within the temperature range. Again, the cooling then took the batch well below the minus 5 degree range and the heating kicked back on again. This back and forth of drastic temperature change was not ideal for temperature control of the batch.

Since the +/- 5° dead band range was too drastic for the process, the range of the +/- was adjusted to 2 degrees Fahrenheit. The tighter temperature range was expected to prevent the jacket temperature from reaching such high and low temperatures before the system would turn over and start heading in the opposite direction. Having the temperature set much closer to the set point ensured that the heating and cooling turned on much sooner. As the temperature rose above the set point within the +/- 2°F dead band, the rate of change was greater than 1 degree per minute in which case the cooling kicked on to slow down the temperature increase. The batch temperature still proceeded to rise above the upper dead band limit and the cooling was activated. The continuous cooling then proceeded to force the batch temperature to drop below the lower end of the dead band. An adjustment had to be made to the rate of change in order to make sure the system did not continue to cool the overall temperature of the batch.

The ideal response was for the jacket to counter-act the cooling from the monomer addition then begin cooling the system once the heat from the reaction took off. Figure 5 below shows how the jacket began heating the batch when the cooler monomer was added then the jacket quickly began to cool once the reaction followed. The jacket remained in full cool because

the glycol had to first cool the walls of the reactor before the emulsion polymerization batch would begin to cool. Once the batch temperature started dropping, the jacket was 20° to 40°F below the batch temperature set point. The jacket then turned into full heat because the batch dropped below the lower dead band. By the time the jacket finally reheated the batch, it had to then begin cooling because the rate of change was too high of a value. Once the batch finally reached the point within the dead band and within a rate of change in the correct plus or minus value, the jacket enters a recirculation mode where no heating or cooling occurs. The batch temperature and the jacket temperature exchanged heat until they are either the same or the batch drops outside of the dead band.

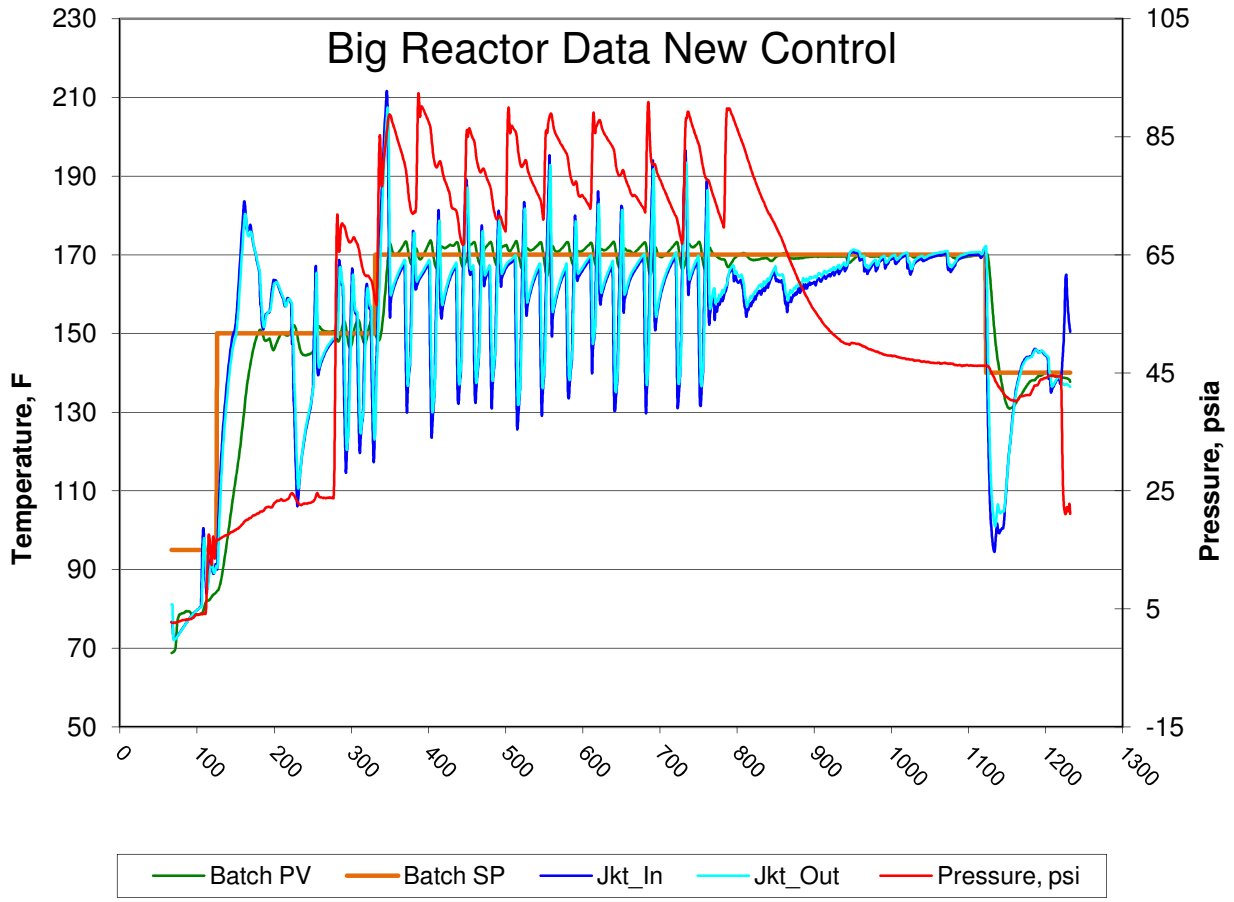

Figure 5. Chart showing the temperature control of an incremental polymerization process. Like the initial chart showing the PID controlled batch, the pressure rises during the monomer addition and declines as the polymerization reacts out. The new control method heats the batch as the cooler monomer is added then instantly begins cooling as the exothermic reaction takes off

in the vessel. The temperature of the batch drops below the lower dead band and the jacket begins heating again until it raises the batch within the dead band. The jacket closes all cooling and heating in the TCU and re-circulates the glycol in the jacket which leads to the jacket and batch temperatures nearing each other.

A zoomed in view of the monomer additions can be seen in Figure 6 below. The closer view of the monomer addition makes it easier to observe when the addition is made and when the reaction takes place. Two incremental charges are made in this figure and they can be seen at the ~385 minute mark and the ~445 minute mark. The set point of the batch is at 170°F and the green line is the present batch temperature. At the two indicated monomer additions, the batch temperature begins a downward direction while the pressure makes a steep vertical climb. The rate of change control mode begins heating the jacket which in turn starts heating the batch. As the exotherm from the reaction picks up, the batch is already above the set point and the jacket then turns to cooling. A lag between the times the batch starts to cool after the jacket cools is seen around the 400 minute mark. The lag increases with the size of the reactor so that production reactors see a much larger lag than those seen by the trend below. The jacket drops 40°F below the set point of the batch and the jacket turns into recirculation mode.

Four black circles exist on figure 6 which show the full heating, full cooling, recirculation, and the rate of change forcing a full cool. Circle 1shows the batch temperature dropping below the dead band and the jacket turning on full heat to raise the temperature of the batch. Circle 2 shows the batch temperature being within the dead band and the jacket is sitting in recirculation mode. The jacket temperature slowly rises in an almost linear fashion as the temperature of the batch remains relatively consistent. Circle 3 shows the result from the jacket being in full heat and the exothermic reaction kicking in. The temperature of the batch begins to rise as the full heating jacket is heating the batch after a monomer addition. Once in the dead band, the ROC is too high and the jacket turns to full cooling. The batch cools until the ROC is within its limits and briefly turns to recirculation mode before having to return to full cooling as the exothermic reaction raises the batch temperature even more. Circle 4 shows how the batch temperature rises too high forcing the jacket to turn onto full cooling and reduces the batch temperature.

The recirculation mode is where the jacket temperature reaches its minimum then gradually rises around 410 minutes. The batch temperature still continues dropping during this sequence and falls about 5°F below the set point until the heating turns the direction of the batch and it approaches the set point again. The effects from the rate of change can be seen around the 410 minute mark. The jacket is heating up the batch but once the batch enters into the dead band limits, the jacket starts cooling again. This cooling happened because the rate at which the batch was heating was greater than 1° per minute and the jacket cooled the jacket glycol to avoid heating. Once the rate of change was in the correct range and the temperature was also within the dead band, the batch turned back into recirculation mode where the batch temperature closely tracked the set point.

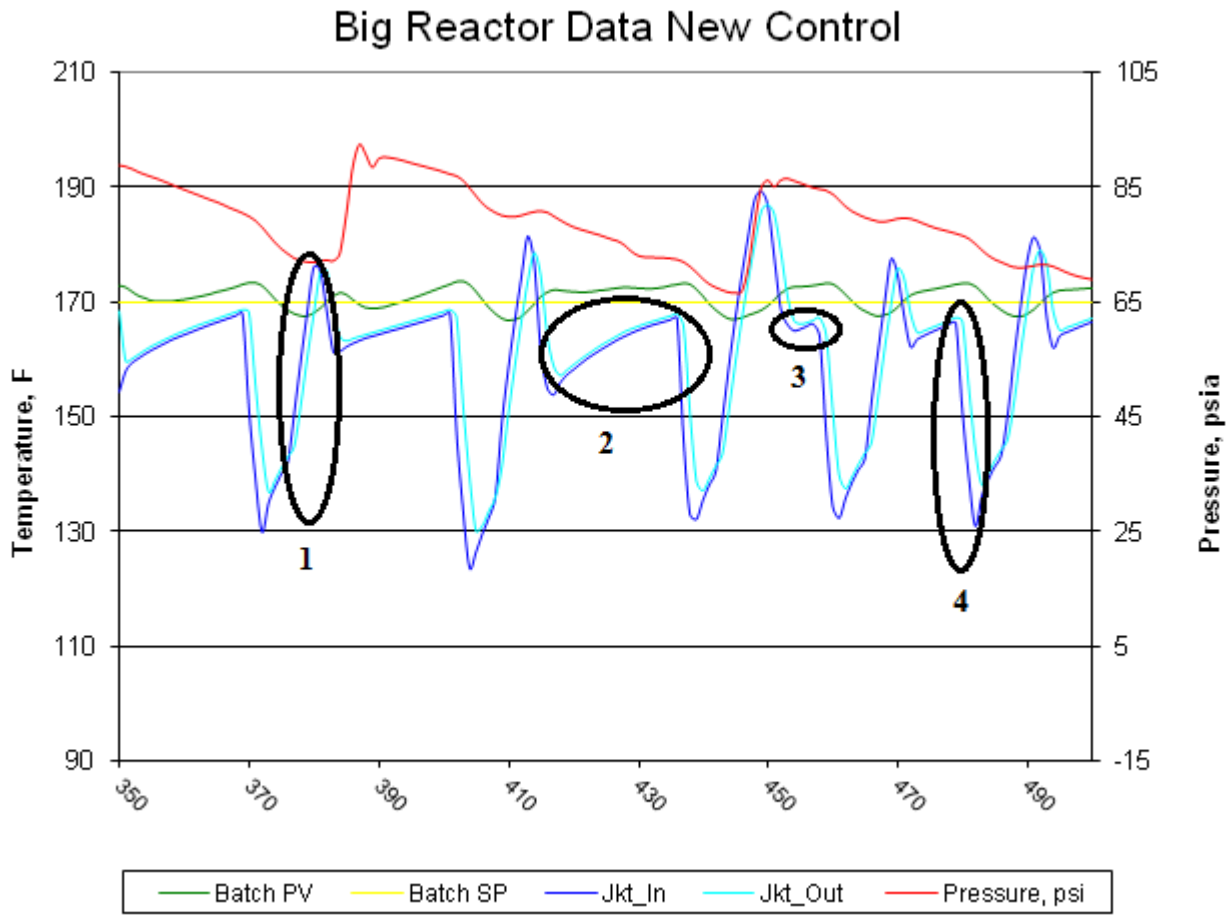

Figure 6. The batch trend below shows how the jacket control method helped to more closely track the set point of the batch. When the incremental charge is made around the 385 minute mark, the batch

temperature drops. The reaction proceeds and the pressure begins to drop. The exothermic reaction heats the batch and around 400 minutes the batch temperature rises above the upper dead band limit. The jacket then turns into full cooling to lower the batch temperature. A lag exists between when the jacket starts cooling and the batch starts cooling as well. This lag increases with the size of the reactor so that during large production batches, the lag time can affect how long the batch takes to heat and cool. The jacket remains in full cool until the batch falls within the dead band limits. The jacket then stops cooling and enters recirculation mode. However, the jacket is too cool and the batch falls below the lower limit of the dead band. The jacket is then heated to heat the batch and the lag occurs again. Once the batch is back in the dead band, the jacket then has to cool because the rate of change is too high and the batch would keep heating. The jacket cooled and the rate of change was reduced so the jacket was able to enter again into recirculation mode where the batch closely tracks the set point.

Four black circles exist on figure 6 which show the full heating, full cooling, recirculation, and the rate of change forcing a full cool. Circle 1shows the batch temperature dropping below the dead band and the jacket turning on full heat to raise the temperature of the batch. Circle 2 shows the batch temperature being within the dead band and the jacket is sitting in recirculation mode. The jacket temperature slowly rises in an almost linear fashion as the temperature of the batch remains relatively consistent. Circle 3 shows the result from the jacket being in full heat and the exothermic reaction kicking in. The temperature of the batch begins to rise as the full heating jacket is heating the batch after a monomer addition. Once in the dead band, the ROC is too high and the jacket turns to full cooling. The batch cools until the ROC is within its limits and briefly turns to recirculation mode before having to return to full cooling as the exothermic reaction raises the batch temperature even more. Circle 4 shows how the batch temperature rises too high forcing the jacket to turn onto full cooling and reduces the batch temperature.

4.0 Temperature Limits on the Jacket

While adjusting the rate of change and the temperature dead band of the batch helped greatly improve the batch temperature tracking the desired set point, improvements still needed to be made to reduce the extreme cold and extreme hot jacket temperatures. The jacket was reaching temperatures 50° to 70° below the batch set point before the batch temperature fell within the dead band around the set point. At this point the jacket would go into recirculation mode at such a cold temperature that the temperature would continue to fall below the lower end of the dead band. The heat would then kick on for the jacket but the batch temperature would drop well below the ideal set point before heating again. The heat would stay on and cause the batch to rise above the upper dead band and the whole heating and cooling process would repeat. Figure 7 below shows how the jacket responded during the heating and cooling before any additional fix was created.

In order to fix overheats and under heats, a clamp on the jacket was needed to ensure the jacket would not continue to fall too far below the lower dead band of the batch temperature and take a long time to heat the system back up to the set point. In order to ensure the jacket would not drop too low, the minimum temperature difference had to be calculated using the heat transfer between the jacket and the polymer batch. The equation for conductive heat transfer helped to calculate the desired temperature difference between the jacket and set point for the jacket clamp. The equation is:

$$Q = m * Cp * \Delta T$$

Q is the amount of heat added to the system, m is the mass, Cp is the specific heat, and ΔT is the difference in temperature. The heat balance determined what the deviation of the reactor jacket would need to be to balance the difference between the heating and cooling dead bands. The

specific heat of the jacket contents is very similar to water which is 1 btu/lb. The latex in the reactor has a specific heat of 0.8 btu/lb. The reactor volume was estimated to be 500 gallons which is about 4500 pounds. The jacket volume was about 120 gallons. The ideal temperature difference was calculated to be 14.46°F. The jacket being 14.46°F below the set point would allow the batch to still be cooled while also making sure the batch was within the dead band and would not drop too far below the set point if the jacket was still 40°F below the set point. Table 1 below shows the results of the calculation for the deviation in jacket temperature.

Table 1. Deviation of jacket from dead band limit.

Reactor Volume (gallons)	500
Mass (pounds)	4500
Jacket, TCU, and piping Volume (gallons)	120
Ratio of Jacket, TCU, and piping to Reactor	24%
Heating dead band (°F)	2.0
Cooling dead band (°F)	2.0
Deviation between heating and cooling dead band (°F)	4.0
Batch Temperature (°F)	170
BTU	14400
Deviation from lower dead band limit (°F)	14.46

After experimenting with the new 14.46° difference as the temperature clamp for the jacket, it was determined that not enough cooling was reaching the reactor and the batch temperature elevated above the set point. Additional experimentation on the ideal jacket clamp was tested and it was determined that 17.5°F above and below the set point was the optimal

setting to improve temperature control. Rarely did the jacket travel too far above the set point for heating purposes because of the exothermic reaction generating heat for the batch. The larger production vessels will require a calculation to determine the ideal clamp on the jackets as well because the size of the vessel compared to the jacket is so much greater at a larger scale.

A close look at figure 7 shows 6 incremental charges of an emulsion polymerization batch which help to emphasize the tracking of the set point by the batch temperature using the new control method. From minutes 300 to about 400 the old PID control method is being used on the polymer batch. The temperature of the batch swings nearly 10°F on multiple occasions with the PID control. One such example of the temperature difference being so large is from about 350 minutes to 390 minutes. During this span a monomer charge had just taken place which can be noted from the instant rise in pressure. The batch temperature increased from the exothermic reaction and reached a maximum temperature of about 164°F. The jacket is cooling the batch to counteract the exotherm and as the reaction takes place, the temperature begins to drop. The temperature of the batch continues to drop and the jacket is still about 10°F colder than the batch when the next monomer charge is added around the 390 minute mark. The colder monomer drops the temperature of the batch even more and the batch reaches a low of about 155°F before the exotherm from the reaction heats the batch. The jacket only momentarily rises above the batch temperature before it once again begins to cool.

Around the 400 minute mark the batch is converted to the new temperature control method which utilizes the rate of change, the varying jacket modes, and the jacket clamp. Using this method, the batch temperature can be seen tracking the set point more accurately as the mode is given time to take control of the batch. The new control with a jacket clamp instantly switches over to recirculation mode once it is turned on. This can be noted by the jacket

temperature forming a slightly curved, upward trend. The new control method on the batch below started at 25°F below set point as the clamp for the jacket temperature. This clamp was adjusted around the 575 minute mark to 20°F deviation from the set point as the clamp on the jacket. The temperature control was greatly improved under the new method which generates a maximum difference of about 3°F during the monomer addition at the 575 minute mark. At the point the monomer is added at the 575 minute mark, the jacket goes into heating mode to counter-act the cooler monomer entering the vessel. The batch temperature dips slightly to about 158°F and the exotherm occurs. During the exotherm, the jacket responds by turning to cooling then heating then cooling again. The batch temperature barely rises above the set point then the jacket turns into a series of recirculation and cooling which keeps the temperature of the batch within a degree or two of the set point through the reaction.

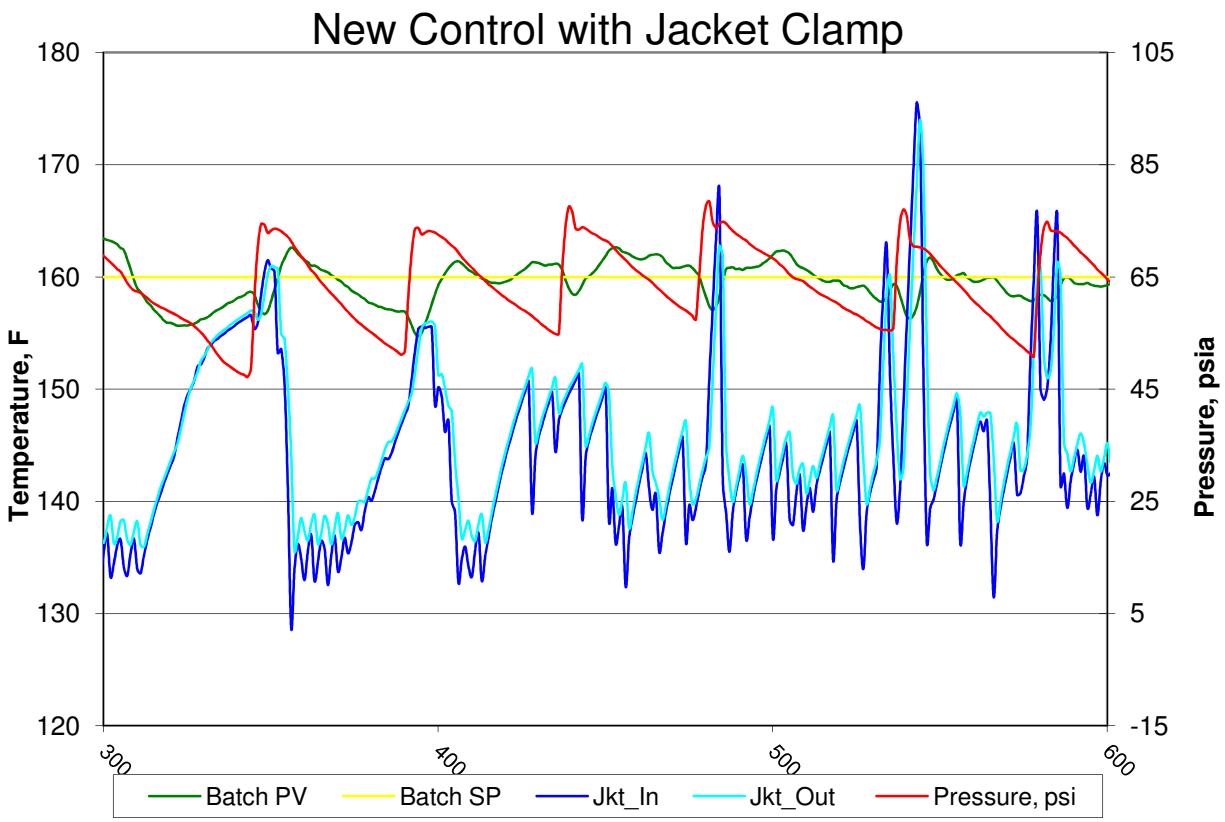

Figure 7. The figure shows an up-close view of the batch trends comparing the PID mode of temperature control and the new ROC, varying heat/cool/recirculation, and jacket clamp mode of temperature control. Minutes 300 to 425 show the PID mode of temperature control. The batch temperature greatly drops below and rises above the set point as monomer additions occur and the exotherm generates heat. 425 minutes to 575 minutes shows the new temperature mode with a jacket clamp at +/- 25°F. The temperature of the batch is more accurately tracking the set point in this mode but still has some variation. The clamp on the jacket is adjusted to 20°F at 575 minutes which then shows the batch following the set point to within a couple degrees Fahrenheit. The use of recirculation allows for the jacket to remain idle in heating and cooling allowing heat transfer to dictate the temperature of the batch without over-cooling or over-heating the batch.

5.0 Control Scheme

The main idea behind the control scheme for the new temperature control method is to use the batch set point, batch temperature, and ROC to determine the action of the vessel's jacket. The jacket would have several parameters that also need to be met in order to determine if the TCU would heat the glycol in the vessel's jacket, cool the glycol in the vessel's jacket, or remain neutral in a recirculation mode that provides no heating or cooling of the glycol. The parameters for the TCU heating and cooling came from experimenting with emulsion polymerization batches at the pilot scale to determine the ideal rate of change limits, the dead band around the batch set point, and the jacket clamp.

Table 2 is an "if-then" table describing the various situations that may occur during an emulsion polymerization batch and the action of the TCU to return or maintain the batch temperature to the batch set point. The goal of the control expression is to ensure the batch temperature does not deviate too much from the set point from the various factors in the incremental emulsion polymerization batch. Factors such as monomer addition, heat of reaction, and the environment can all play a role in affecting the temperature of the batch and the new control scheme was developed to minimize the temperature swings seen from PID control. The rate of change for the batch was set at + 1°F per minute for heating and -0.5°F for cooling. The dead band around the batch set point was set at +/- 2°F. The clamp on the jacket was set at +/- 17°F of the set point.

Table 2. Table of the various situations within an emulsion polymerization batch that arise during production and the response by the new control mode to minimize deviation of the batch temperature from the set point of the batch. The ROC was + 1°F per minute for heating and -0.5°F for cooling and the dead band was set at +/- 2°F. The clamp on the jacket fluid was set at +/- 17°F of the batch set point.

IF	THEN
Batch temperature is within +/- 2°F of the set point & ROC is less than + 1°F per minute for heating and -0.5°F for cooling	Recirculation mode is on, cooling is off, and heating is off.
Batch temperature is within +/- 2°F of the set point & ROC is greater than +1°F/min of the set point	Cooling is activated on TCU, heating is off
Batch temperature is within +/- 2°F of the set point & ROC is greater than -0.5°F/min of the set point	Heating is activated on TCU, cooling is off
Batch temperature is greater than +2°F of the set point	Cooling is activated on TCU, heating is off
Batch temperature is greater than 2°F below the set point	Heating is activated on TCU, cooling is off
Jacket fluid temperature reaches 17°F below the set point during cooling	Cooling is turned off, heating remains off, Recirculation mode is on
Jacket fluid temperature reaches 17°F above the set point during heating	Heating is turned off, cooling remains off, Recirculation mode is on

If any of the conditions are met on the left side of the table, then the response on the right side of the table would occur. The primary factor for determining the action of the TCU was the batch temperature. The batch temperature was looked at first followed by the rate of change. If the batch temperature was outside of the dead band limits of +/- 2°F then either heating or cooling would be activated. Once the batch temperature fell within the dead band of the set point, the system then looked at the ROC. If the ROC was too high, then the TCU would respond by trying to slow down the ROC by either heating or cooling the system. Making sure the ROC was not too high ensured the jacket did not continue heating or cooling the batch too much causing a series of spiked heating and cooling trends with greater fluctuations in batch temperatures.

The jacket clamp was used primarily to prevent the batch from cooling too much. The system responded faster to the steam heating than it did to the cooling water. This meant that the cooling water would continuously drop in temperature before the emulsion polymerization batch would begin to drop and the glycol would be 50°F or 60°F below the batch temperature when it finally started to cool. This led to the batch temperature cooling too much and the heating would not be able to recover quickly enough before the batch temperature had already dropped well below the lower dead band.

6.0 Results

The new control method combining the use of the rate of change, varying modes of heating, cooling, and recirculation, and clamping the jacket has generated a functional temperature control method for a pilot scale incremental polymerization batch. Additional testing is required on the new method of temperature control in order to confirm that the method is effective for the numerous variations of incremental batches being used in industry today. The PID mode is able to handle the consistent reaction rates because of the minimal disturbances in the batch leaving the new method of temperature control to be most effective on the incremental polymer batches.

The parameter for the temperature control scheme of an incremental batch system was designed as follows:

1. Cooling offset 17.5 F
2. Heating temperature deadband 2.0 F
3. Cooling temperature deadband 2.0 F
4. ROC cooling start 0.50 F/min
5. ROC heating return 0.50 F/min
6. ROC cooling return -0.15F/min

Once further testing has been completed on the temperature control method and it is assured to work on the pilot scale, the control scheme can then begin the process to being implemented in a production facility. The new system may take a few trials to perfect the jacket clamp temperature and rate of change parameters so it is suggested that the control mode be tested on a polymerization batch that can withstand greater fluctuations in temperature without greatly affecting product quality. The raw material and energy costs for running a production batch can be high so it is important to minimize the potential for losses in materials and energy. If the system is effective and efficient in a production facility, the resulting polymer products will have fewer variables to cause problems and affect the final product quality.

7.0 Sources

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